Progress Report (2nd quarter)

Advanced Lubrication for Energy Efficiency, Durability and Lower Maintenance Costs of Advanced Naval Components and Systems

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Abstract

In boundary lubrication, spacing of mating surfaces in direct physical contact is in the scale of surface asperities. These conditions may benefit from the nanoscale dimension of the advanced nanoparticle lubricants in the following ways: (1) by supplying nano to sub-micron size lubricating agents which reduce friction and wear at the asperity contact zone, (2) by enabling strong metal adsorption and easy wetting, (3) by reacting with the surface to form durable lubricating "transient transfer" films, sustain high loads and also retain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety. These materials specifically designed on antiwear and extreme pressure chemistries can significantly lower the sulfur and phosphorus level in the lubricant additive, and therefore provide environmental benefits.

The project encompasses a detailed investigation of advanced nanolubricants (NanoGlide®) that favorably impact robust boundary film formation to reduce wear and friction. These active nanolubricant additives are designed as surface-stabilized nanomaterials that are dispersed in a hydrocarbon media for maximum effectiveness. This effort is focused on developing active nanoparticle composites, optimize process design, physical and chemical characterization of nanomaterials, detailed tribological film characterization, and tribological testing to document friction and wear improvements.

Contents

Summary

In this project we are developing extreme-pressure additives based on surface modified nano molybdenum sulfide (MoS_2). These additives are based on “green” surface chemistries used in the food industry combined with modified nano molybdenum sulfide and will have application in the many heavy duty lubrication systems used by the Navy, imparting lower friction, higher reliability and longer life, leading to reduced energy usage and increased mission availability. They will also have potential for use throughout commercial industries.

In the second quarter of this project, developed nanolubricants were selected and synthesized for application as additives in motor oils, gear oils and greases. Synthesis, characterization, and optimization of developed nanolubricant formulations (NanoGlide®) prepared by laboratory bench process were finalized. Properties of these nanolubricants were investigated through chemical, structural, and tribological analysis.

NanoGlide® production procedures and Design of Experiments (DoE) for synthesis and optimization using scale up were developed. De-agglomeration and optimization studies of synthesized nanolubricant formulations are in progress and on schedule for process scale up and nanomanufacturing of NanoGlide®.

Design of experiments for tribological testing of nanolubricant in motor and gear oil, and greases was also developed and finalized. Tribological testing of NanoGlide® samples in motor oils using 4 ball test, EP 4 ball test was performed, and their performance, comparison, and evaluation are presented and discussed in this report. The feasibility lubrication testing of NanoGlide® samples in military oils was evaluated using WAM test and competition/synergy between additive package in formulated military-certified oils and nanoparticle additives was explored. Design of gear testing (FZG test) and parts list of the required main materials for the set up is developed and is in the process of building.

The project is on track.

Introduction

This project focuses on development of challenging but high-payoff applications for the active family of nanolubricant additives, which is called NanoGlide® [1, 2]. In previous work, NanoMech has explored the fundamental science of nanoparticle design and synthesis using a top-down nanomanufacturing process, including the mechanisms of synthesis, interaction of “simple organic and inorganic materials” for deagglomerated nanostructures, dispersion stability, and preliminary tribological behavior, and promising results have been observed that give a solid foundation for realistic and valuable application-specific product development [3]. Now the challenge is to experiment further with this concept to apply the underlying science in investigating the feasibility of

NanoGlide application for preferred and versatile materials that are of importance and use in the current lubricant technology.

The findings from NanoMech's preliminary studies are of significant importance in the development of active nanoparticle-based lubricants, with outstanding lubrication properties responding to extreme pressure (EP) and related transient high temperature conditions [4], and at the same time, environmentally acceptable at low cost required in applications where boundary layer lubrication is crucial.

Project Objectives

The high-level objective of this project is to develop nanoparticle-based additives to improve friction and wear characteristics of naval components and systems with a focus to enhance durability, energy efficiency, and maintenance costs of them.

For this project, NanoMech follows technical tasks that are based on the project research plan (see Appendix, Table A1):

1. Design of application-specific active nanolubricants (NanoGlide®);
2. Process scale up and nanomanufacturing of NanoGlide®;
3. Synthesis, de-agglomeration and optimization of NanoGlide®;
4. Structural, chemical and physical analysis of NanoGlide®;
5. Tribological testing of NanoGlide®;
6. Commercialization of NanoGlide®.

Project Scope

In this project quarter, the interaction of developed formulations (see 1st quarter report) were studied to distinguish the effects of these unique additives in providing reduced friction and wear, and explore synergy and/or competition with the complete formulation package. Therefore, understanding the role of each component in the formulation with nanoparticle additives is critical and needs systematic studies.

The effort also included development, optimization and scale up of a chemo-mechanical process to generate multi-component nanoparticle additive systems that are suitably stabilized and dispersed in oil. Extensive laboratory-based tribological evaluation of nanomaterials is in progress to evaluate friction and wear characteristics in boundary lubrication regime using pin on disc, 4 Ball and Extreme Pressure 4 Ball tests.

Physical and chemical characterization of these materials is been performed using a range of microscopic and surface analytic tools (TEM, EDX, XRD, and SEM). The focus is on understanding the inorganic-organic interface chemical behavior resulting in surface lubrication, dispersion in hydrocarbon media, and formation of tribofilm at the friction points. Specimens from tribotesting have been collected and preserved for tribofilm analysis (XPS, Auger and FIB/EDX).

Following laboratory tribological test results, the additives were screened using WAM Scuffing Load Capacity Tests to evaluate preliminary performance of NanoGlide in military certified oils.

Major Activities

The research activities as outlined in the project plan (2nd quarter, Table A1) for the funding phase February 20, 2009 – May 20, 2010 are noted below. The major activities of the team during this reporting period are:

Task 1. ***Designing of application-specific active nanolubricant (NanoGlide)*** (*Timeline for Task 1: November 2009 – August 2010*);

Task 2. ***Process scale up and nanomanufacturing of NanoGlide*** (*Timeline for Task 2: January – August 2010*);

Task 3. ***Synthesis, de-agglomeration and optimization of NanoGlide*** (*Timeline for Task 3: January – August 2010*);

Task 4. Structural, chemical and physical analysis of NanoGlide (*Timeline for Task 4: March – August 2010*);

Task 5. Tribological testing of NanoGlide (*Timeline for Task 5: March – August 2010*).

Specific tasks with timeline for deliverables and milestones to be performed by NanoMech including tasks for the University of Arkansas as a subcontractor and their progress are described below.

Task 1: Designing of application-specific active nanolubricant (NanoGlide®)

(*Timeline for Task 1: November 2009 – August 2010*)

In this task, the project team has already designed the application-specific active nanolubricant that contains inorganic nanoparticles integrated with organic molecular medium to add additional lubrication properties and form protective capping layer to suspend them in base oil medium and protect from sedimentation. Two formulations are in progress of evaluation for lubrication applications (additives to gear and motor oils and greases) and are based on the developed and characterized formulations in the laboratory scale. Molybdenum disulfide nanoparticle forms the inorganic core/carrier integrated with phosphorus-based compounds or environmentally benign vegetable oil/phospholipid molecules in a stable surface stabilized composition.

The nanoparticles include both hard, durable, load carrying components like phosphate layer which can react with mating parts at high temperatures and softer, easily mechanically shearable components, pressure sensitive deformable (exfoliable) MoS_2 nanoparticles and resulting transfer film, along with organic integrated canola oil fatty acid chains and phospholipids. The experimental procedures were described in the 1st quarter report, and detailed information on the synthesis can be found in patent applications [1, 2].

These developed nanolubricants could address the diverse application needs of the Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to “dry and harsh” conditions and deliver tribofilm as a result of plastic deformation, when trapped among asperities. Such application components of interest to the Navy, for on- and off-shore purposes, are bearings, gear boxes, and engines (see Task 5 “Tribological testing of NanoGlide” of this report).

Deliverables

Accomplished deliverables:

1. Design of application specific active nanolubricants of interest to the Navy and potential Navy customers/collaborators;
2. Materials for synthesis of nanoparticles selected for application as additives in gear oils and greases.
3. Synthesis and optimization of developed nanolubricant formulation by lab scale;

Deliverables for 3rd quarter of the project:

1. Structural, chemical and physical analysis of developed nanolubricant formulation.

Task 2: Process scale up and nanomanufacturing of NanoGlide®

(*Timeline for Task 2: January – August 2010*)

The process scale up is one of the major tasks to explore for this project period. The objectives of the scale up process were obtaining higher process yield in a pilot scale industrial process, low and affordable cost and the development of protocols for safe handling of the active EP-EA material in large quantities.

The laboratory bench and pilot scale production mills have been used for particle size reduction and chemo-mechanical milling with the surrounding medium such as organic molecules. The Design of Experiment (DoE) approach is used to optimize the scale up processing to achieve the outcome of similar morphological properties of samples synthesized in laboratory scale and to obtain optimal milling parameters in pilot scale mill processing. During the synthesis and optimization process, the main objectives are: 1) reduction of synthesis time, 2) predictability in particle size, 3) nanoparticle capping consistency, and 4) avoiding agglomeration of nanoparticles.

The nanoparticles samples were collected for variable parameters following the DOE matrix and will be used for optimization of NanoGlide® synthesis and de-agglomeration studies.

Deliverables

Accomplished Deliverables:

1. Production mill for scale up is installed and in use;
2. Milling media were selected and purchased;
3. Synthesis of developed nanolubricant formulations by production mill scale;
4. Design of Experiments is developed and used for optimization of scale up process.

Deliverables for 3rd quarter of the project:

1. Optimization of synthesized nanolubricant formulation for scale up in combination with Task 3;
2. De-agglomeration studies of synthesized nanolubricant formulation in combination with Task 3.

Task 3: Synthesis, de-agglomeration and optimization of NanoGlide®

(*Timeline for Task 3: January – August 2010*)

In the proposed research, we will initially use lab-scale and then move up to large scale processing equipment at NanoMech to perform the synthesis, adjusting each of the critical variables in a Design of Experiment (DoE) approach to optimize the interdependent parameters. The deliverable from this task will be samples of the synthesized nanolubricant additive.

Results and discussions

The following update is mainly focused on the feasibility experiments and results based on the hybrid milling for synthesizing MoS_2 nanoparticles involving mechanical shearing process. The outcomes of this exploration are narrowed particle size distribution and shortened process time that contributed to the technical objective of extended shelf life and suspension stability, and the commercial goal of increasing yield per batch with significant reduction of the processing time.

The advantages of this hybrid process are that it not only reduces the particle size, but also retains the crystalline character of the MoS_2 particles. The process largely prevents crystal structure breakdown (amorphization) and lattice defects that are prone to occur in a high-energy mechanical shearing process if run for significantly extended time without strictly controlling the gas environment.

For process optimization, the MoS_2 powder is planned to be chemo-mechanically milled for various time conditions, variable ball-to-powder ratios, and under various ambient conditions, starting with air, vegitable oil, thiophosphate, phospholipid and the subsequent combination of milling in air followed by milling in organic agents. The oil medium in the selected combination will be chosen to allow (a) homogeneous dispersion of particles inside the milling vial, thus avoiding particle clogging (b) utilizing mechanical energy to forge interaction between MoS_2 and organic agents to provide capping and integration of organic molecules in MoS_2 nanoparticles and (c) capping with organic molecules, reduced agglomeration and preparing a uniform dispersion with the base oil.

The particle size of each batch of milled sample will be analyzed by use of a particle size analyzer, and the particle morphology will be analyzed using SEM and/or TEM. Based on the particle size differences, sedimentation rates, and agglomeration, the results for process optimizations will be compared and presented in the next reporting phase (second quarter report).

Deliverables

Accomplished deliverables:

1. Design of experiments for synthesis and optimization for scale up;
2. Development of NanoGlide® production procedure (also see 1st quarter report).

Deliverables for 3rd quarters of the project:
1. Development of product control procedures;
2. Synthesis of nanolubricants for naval applications;
3. Optimization of scale up milling.

***Task 4*: Structural, chemical and physical analysis of nanostructures and inorganic-organic interfaces**

Complementary analytical techniques are applied with particular objectives to study properties of synthesized nanoparticles and scale up optimization (size and shapes, surface area, nanostructure, and chemical analysis) and tribological performance (tribofilm formation, debris formation, nanoparticles morphology).

Results and Discussions

Nanoparticles were studied using transmission electron microscopy (TEM). TEM graphs of bulk MoS_2 and synthesized nanoparticles are compared in Figure 1 and reveal significant size decrease and formation of ellipsoidal MoS_2 nanoparticles.

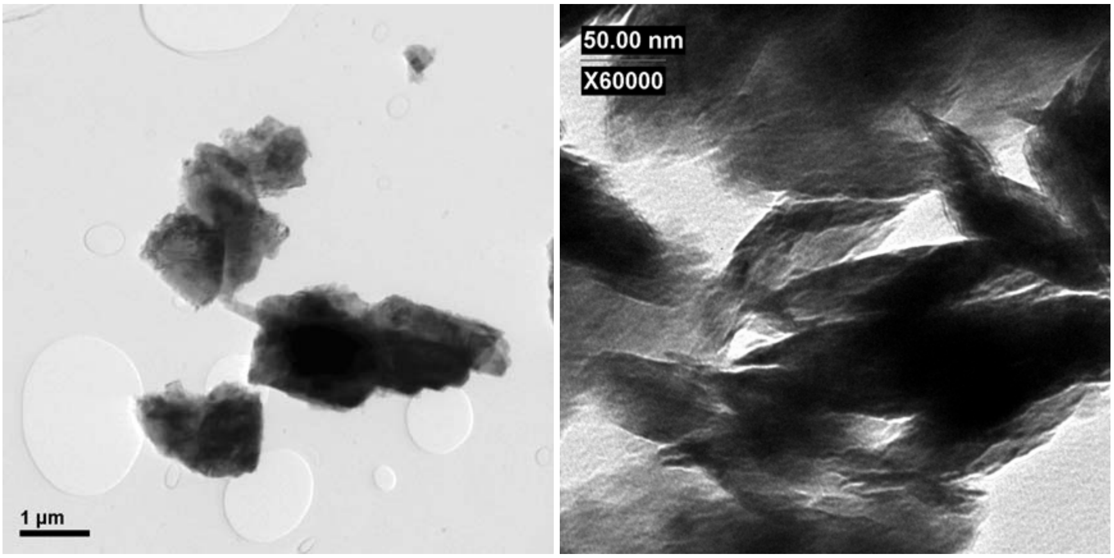

Figure 1. TEM graph of bulk MoS_2 (left) and HRTEM of MoS_2 nanoparticles (right)

TEM results are confirmed by chemical composition of MoS_2 from EDX studies (Figure 2) and XRD studies that reveal a significant decrease of sizes during nanoparticles preparation process (Figure 3).

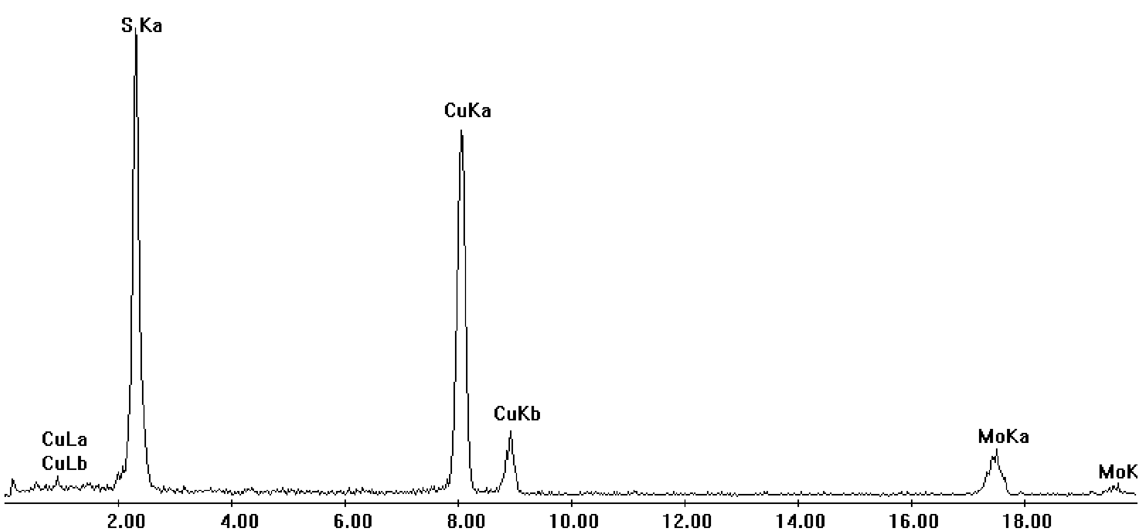

Figure 2. EDX spectra of MoS_2 nanoparticles (distinctive peaks of Mo and S of molybdenum sulfide pattern, Cu signal is from TEM grid)

X-ray diffraction (Rigaku D/Max) with Cu-Kα radiation was used for the phase change analysis and size estimation for lab scale prepared MoS_2 nanoparticles. Laboratory bench prepared samples for different time periods with 6 hours increment were studied and compared with commercially available MoS_2 (Figure 3 of this report). Longer time synthesis broadens XRD peaks and decreases particle sizes from bulk particles (3.5 µm, average size) to nanoparticles (70 nm, average size) correspondently.

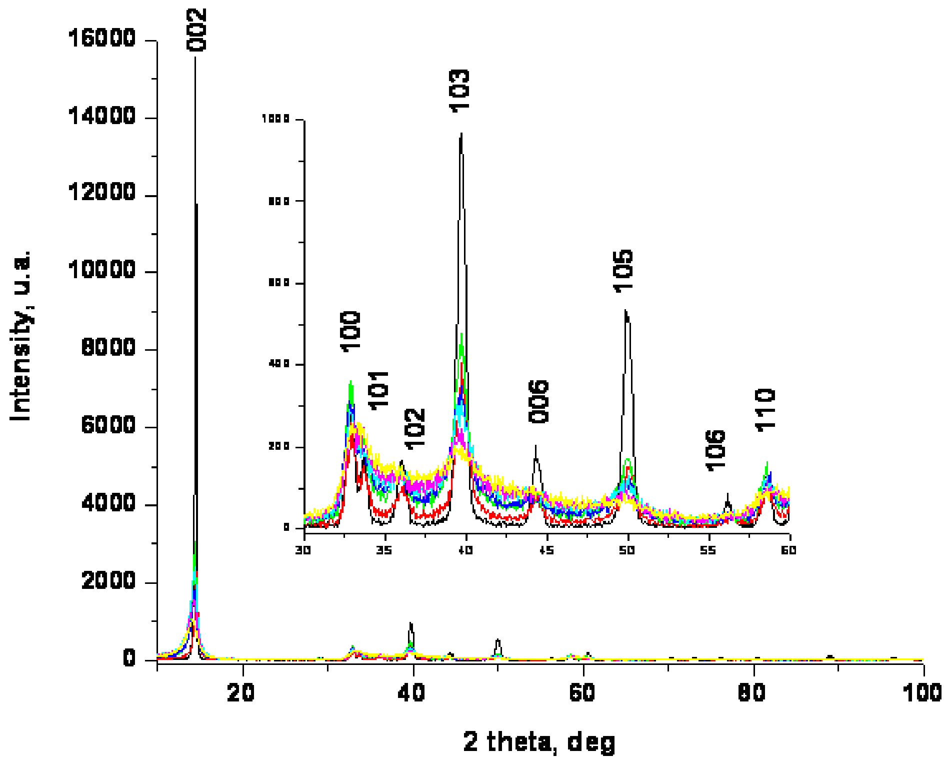

Figure 3. Powder XRD of MoS_2 samples

While XRD gives only average size of primary particles (crystallites), laser scattering techniques (particle size analyzers) can study size distribution and agglomerate sizes for primary and secondary particles. Laser scattering technique may be useful to study dispersion and stabilization of MoS_2 nanoparticles in base oil. It was found that lab scale samples contain two fractions of particles. One fraction is the primary particle and second fraction has secondary particles (aggregates of primary particles) (Figure 4).

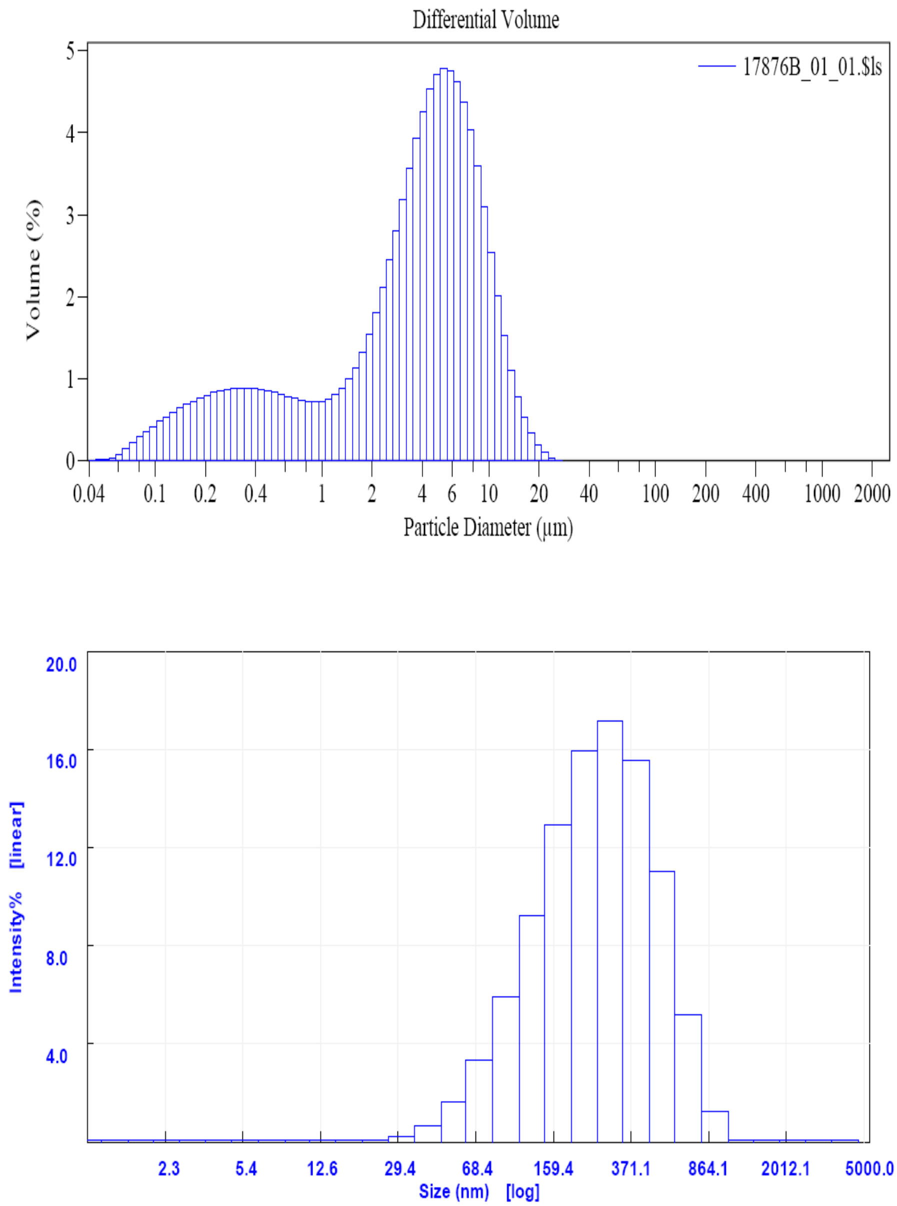

Figure 4. Particle size distributions of primary and secondary particles (top) and primary particles (bottom) for MoS_2 sample in PAO oil

These studies are used to find out the best suitable procedures for de- agglomeration, dispersion in oil media to study their sedimentation properties and capping of nanoparticles with protective layer to protect from aggregation.

XPS, Auger, and TOF-SIMS, SEM, and EDX analysis will be used for morphological and chemical analysis of wear tracks after tribological testing to study tribofilm formation by nanoparticles on specimen. Analytical techniques will be used after tribological testing (see Task 5) to study: wear surface morphology, chemistry and elemental distribution on wear tracks, properties of various transfer layers on mating parts and other reaction products, and size, morphology and surface chemistry of the debris.

Deliverables

Accomplished deliverables:

1. Characterization of NanoGlide® nanolubricants prepared by laboratory bench process;

2. Fundamental understanding of nanolubricants prepared by laboratory bench process through chemical, structural, and tribological analysis.

Deliverables for 3rd quarters of the project:

1. Characterization of NanoGlide® nanolubricants prepared by scale up process;

2. Fundamental understanding of nanolubricants prepared by scale up process through chemical, structural, and tribological analysis;

3. Morphological and chemical analysis of tribofilms.

Task 5: Tribological testing

Fundamental and applied research will be conducted using bench-top tribological test setups (*pin-on-disc, four-ball, extreme pressure four ball test, WAM*) at varying loads, speeds to identify the behavior of these under different lubrication regimes (Stribeck curves), particularly focusing on the boundary lubrication conditions.

5.1 Tribological performance of nanolubricant in motor oils

The lubrication performance of various oils (motor, gear oils) and greases with MoS_2 nanoparticle (NanoGlide®) additives will be studied through tribological testing. The test results will be used to generate friction and wear maps demonstrating the useful tribological performance and compare performance of MoS_2 nanoparticles in oils with base oils (non-formulated and formulated oils). The tribological testing and tribofilm analysis will clarify the behavior of each component in the oil blend, explaining the possible synergistic or antagonistic effect among them. This study will be the key observation in designing and developing the final nanoparticles based formulation for use in applications.

In this reporting period, MoS_2 nanoparticles (1% wt.) were added to motor oil (neat, formulated complete, and formulated oil without friction modifier) to evaluate and compare their performance (10 samples in Table 1) in higher viscosity motor oil “A” and lower viscosity motor oil “B.” The formulated oil without friction modifiers (thiomolybdate based additive) was specifically selected to see direct effect of MoS_2 nanoparticle addition on formulated oil. The tribological performance of nanoparticles in gear oils and grease will be reported in the next report period.

Table 1. Motor oil samples for tribotesting

Motor oil Samples:	
1 sample	"A" FORMULA NEAT
2 sample	“B” FORMULA NEAT
3 sample	“A” FORMULA COMPLETE
4 sample	“A” FORMULA MINUS MoS_2
5 sample	“B” FORMULA MINUS MoS_2
6 sample	"A" FORMULA NEAT +NanoGlide
7 sample	“A” FORMULA COMPLETE + NanoGlide
8 sample	“A” FORMULA MINUS MoS_2 + NanoGlide
9 sample	“B” FORMULA MINUS MoS_2 + NanoGlide
10 sample	“B” FORMULA MINUS MoS_2 + nanoWS_2

To compare performance of these motor oils samples, five groups of motor oil samples without and with nanoparticle additives were analyzed (Table 2) using Four ball and Extreme Pressure (EP) Four ball tests. The pin-on-disk and block-on-ring tribotesting of these samples will be provided in the next report period and will be combined with tribotesting results for gear oils and greases.

Table 2. Comparison of tribological performance of five groups of motor oils

Compare tribological performance for motor oil:
1. Motor Oil “A” FORMULA MINUS MoS_2 vs. Motor Oil “A” FORMULA NEAT For baseline data comparison without NanoGlide 2. Motor Oil “A” FORMULA MINUS MoS2 + NanoGlide vs. Motor Oil “A” FORMULA NEAT vs. Motor Oil “A” FORMULA NEAT + NanoGlide For baseline data comparison with NanoGlide 3. Motor Oil “A” FORMULA COMPLETE vs. Motor Oil “A” FORMULA MINUS MoS_2 + NanoGlide vs. Motor Oil “A” FORMULA COMPLETE + NanoGlide For baseline data comparing current offering to proposed NanoGlide formula 4. Motor Oil “B” FORMULA MINUS MoS_2 vs. Motor Oil “B” FORMULA NEAT For baseline data comparing modified viscosity before addition of NanoGlide 5. Motor Oil “B” FORMULA MINUS MoS_2 + NanoGlide vs. Motor Oil “B” FORMULA MINUS MoS_2 6. Motor Oil “B” FORMULA MINUS MoS_2 + NanoGlide vs. Motor Oil “B” FORMULA MINUS MoS_2+ nanoWS_2

The tribotesting of first group is designed to compare base line of motor oils that are non-formulated neat and formulated without friction modifier additives and without nanoparticles additives (NanoGlide®) and results are compiled in Table 3. The Four ball test showed very high coefficient of friction (see Appendix B for coefficient of friction for tested samples) and wear scar diameter for neat motor oil "A" and significant decrease in these values for formulated oil "A" (without friction modifier). The EP Four ball test revealed similar situation for these oils where the load wear index, last non-seizure, last seizure and weld loads were very low for neat oil and significant improvements of load index and loads for formulated oil (without friction modifier).

Table 3. Group 1 tribological performance

Oil	Additive	ASTM D4172 4ball test		ASTM D2783 EP 4 Ball Test (load, kg / scar, mm)			
		WSD, mm	COF	Load wear index	Last non-seizure	Last seizure load	Weld
Motor Oil "A" Neat	-	0.73	0.13	17.21	32 /0.29	100/3.11	126
Motor Oil "A" Formula minus MoS_2	-	0.38	0.1	41.36	100/0.43	160/2.91	200

Addition of MoS_2 nanoparticles (NanoGlide) to neat motor oil "A" has not shown significant improvement for Four ball test due to tribological performances of these oils in hydrodynamic regime lubrication (Table 4). However, EP Four ball test results clearly show advanced anti-wear performance (higher load wear index, last non-seizure over neat oil and higher last seizure load, weld load over neat motor oil "A" and formulated motor "A" (without thiomolybdate).

Table 4. Group 2 tribological performance

Oil	Additive	ASTM D4172 4 ball test		ASTM D2783 EP 4 Ball Test (load, kg / scar, mm)			
		WSD, mm	COF	Load wear index	Last non-seizure	Last seizure load	Weld
Motor Oil "A" Neat	-	0.73	0.13	17.21	32/0.29	100/3.11	126
Motor Oil "A" Formula minus MoS_2	-	0.38	0.10	41.36	100/0.43	160/2.91	200
Motor Oil A Neat	NanoGlide	0.70	0.13	26.16	50/0.34	200/3.28	250

The situation is similar for the Group 3 where hydrodynamic lubrication testing in Four ball test doesn't allow to distinguish between lubrication from oil and nanoparticles (Table

5). However, EP Four Ball test clearly showed that nanoparticles in formulated motor oils (without friction modifiers and with friction modifiers) significantly increased the load wear index, last non-seizure, last seizure, and weld loads in comparison with formulated motor oil ("A" Complete).

Table 5. Group 3 tribological performance

Oil	Additive	ASTM D4172 4ball test		ASTM D2783 EP 4 Ball Test (load, kg/scar, mm)			
		WSD, mm	COF	Load wear index	Last non-seizure	Last seizure load	Weld
Motor Oil "A" Complete	-	0.36	0.075	35.14	80/0.40	160/2.91	200
Motor Oil "A" Formula minus MoS_2	NanoGlide	0.38	0.09	43.53	100/0.43	200/3.02	250
Motor Oil "A" Complete	NanoGlide	0.38	0.08	44.03	100/0.38	200/2.82	250

Motor oils "B" have a lower viscosity in comparison with motor oils "A." The purpose of these studies was to evaluate the performance of nanoparticles in lower viscosity oils and possibility of high viscosity oil substitution with lower viscosity oil without losing lubrication performance (Tables 5 and 6). The Four ball test showed that addition of MoS_2 nanoparticles to motor oil "B" has increased load wear index of motor oil "B" (without friction modifiers) and tribological results for last seizure load and weld load were comparable with results for higher viscosity motor oil "A."

Table 6. Group 4 tribological performance

Oil	Additive	ASTM D4172 4ball test		ASTM D2783 EP 4 Ball Test (load, kg/scar, mm)			
		WSD, mm	COF	Load wear index	Last non-seizure	Last seizure load	Weld
Motor Oil "B" Formula minus MoS_2	-	0.35	0.075	34.45	80/0.41	160/2.79	200
Motor Oil "B" Formula minus MoS_2	NanoGlide	0.39	0.09	36.60	80/0.39	200/3.01	250

Finally, group 5 was used to compare the tribological performance of MoS_2 nanoparticles with performance of commercially available WS_2 nanoparticles. The Four ball test showed lower coefficient of friction and wear scar diameter for NanoGlide and both nanoparticle materials had similar tribological performance for last-non seizure, last seizure load, and weld loads (Appendix B, Figures B.9. and B.10; Table 6).

Table 6. Group 5 tribological performance

Oil	Additive	ASTM D4172 4ball test		ASTM D2783 EP 4 Ball Test (load, kg / scar, mm)			
		WSD, mm	COF	Load wear index	Last non-seizure	Last seizure load	Weld
Motor Oil “B” Formula minus MoS_2	nano WS_2	0.42	0.105	43.54	100/0.42	200/3.29	250
Motor Oil “B” Formula minus MoS_2	NanoGlide	0.39	0.09	36.60	80/0.39	200/3.01	250

Used oils and specimens were collected for morphological and chemical analysis of tribofilms and nanoparticles after tribotesting (See Task 4, deliverable for 3rd quarter).

5.2 Tribological performance of nanolubricant in military oils

Two brands of military certified oils were selected to be used. Oil “M1” (MIL-PRF-23699) is an engine oil and oil “M2” (DOD-PRF-85734) is an aircraft gearbox oil.

WAM Scuffing Load Capacity test (Figure 5) was selected to study feasibility tribological performance of developed NanoGlide formulations. Two WAM High Speed Load Capacity tests for each oil were performed and a third test was terminated at Load Stage 10 to document surfaces.

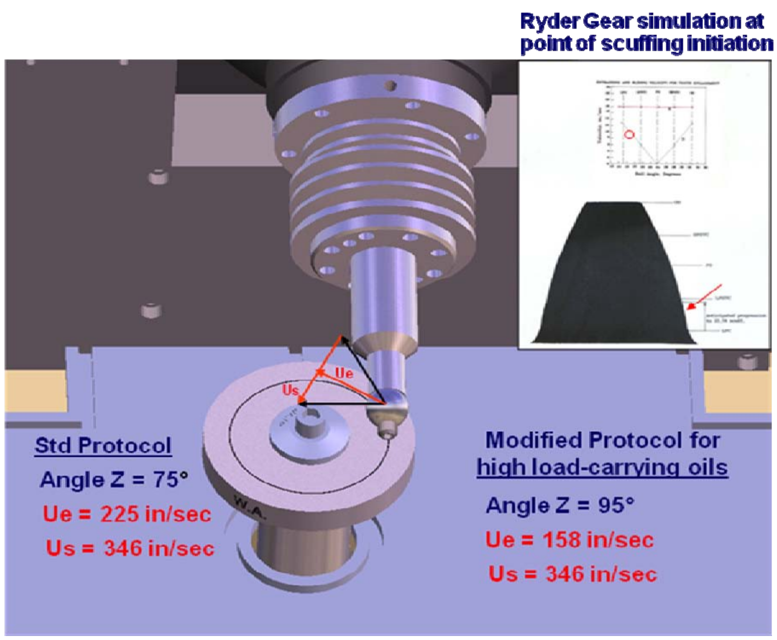

Figure 5. WAM High Speed Load Capacity Test [5]

Military certified oil (M1 and M2) formulations with NanoGlide show similar scuffing performance (average scuffing failure stage) compared to formulations without NanoGlide (Table 7). NanoGlide formulations show different traction behavior reflecting differences in wear behavior (Appendix C, Figures C.1-C.4).

Table 7.Test oils (M1 and M2) with and without NanoGlide

Run File: naa.run				Rolling Velocity: 158 in/sec
Disc: 9310, Ra=6μ-in				Sliding Velocity: 345 in/sec
Ball: 9310, Ra=10-12μ-in				Ambient Temperature
Ball Velocity: 234 in/sec				Velocity Vector Angle (Z): 95°
Disc Velocity: 234in/sec				
			Average	
		Macro-scuff	Scuffing	
Test	**Lube**	**Stage**	**Failure Stage**	**Comments**
WAM81616	M1	19		
WAM81617	M1	16	**17.5**	
WAM81627	M1			Stopped at load Stage 10
WAM81618	M2	20		
WAM81619	M2	19	**19.5**	
WAM81625	M2			Stopped at load Stage 10
WAM81620	M1 + NanoGlide	19		
WAM81621	M1 + NanoGlide	18	**18.5**	
WAM81628	M1 + NanoGlide			Stopped at load Stage 10
WAM81622	M2 + NanoGlide	17		
WAM81623	M2 + NanoGlide	17	**17**	
WAM81626	M2 + NanoGlide			Stopped at load Stage 10

Tests terminated at load stage 10 show the formation of surface films with NanoGlide. These surface films may be derived from MoS_2. SEM surface analysis of the disc specimen tracks show more pronounced fine abrasive wear with NanoGlide than without NanoGlide (Figure 6). Wear is on the order of the roughness features and difficult to quantify.

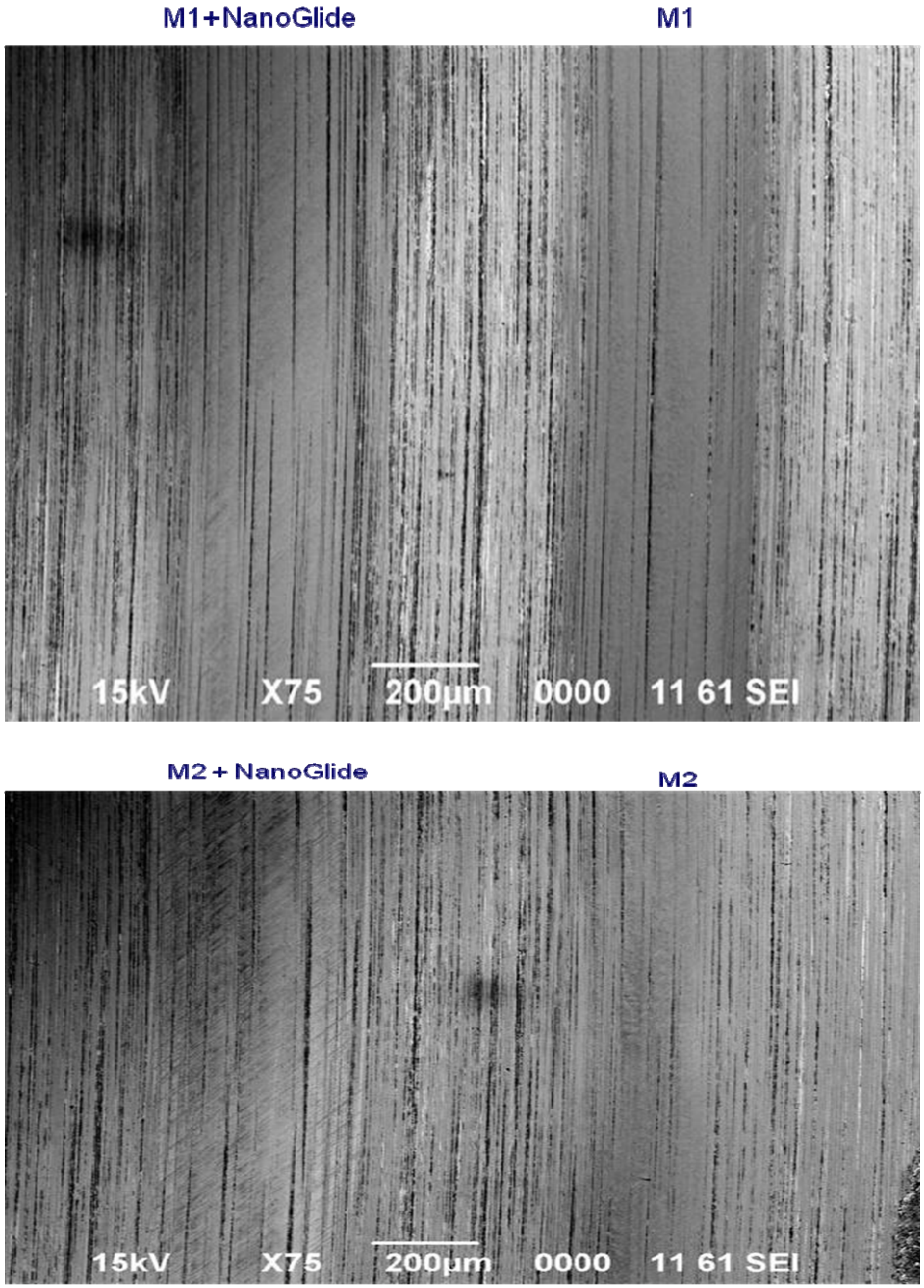

Figure 6. SEM analysis of test tracks on disc specimen: top - M1 oil and M1 oil + NanoGlide; bottom – M2 oil and M2 oil + NanoGlide

From feasibility testing, it was postulated that NanoGlide chemistry may be competing with the anti-wear and EP additives in the reference oils and optimization and adjustment in chemical composition needs to be performed to eliminate the competition between additives in formulated oils and nanoparticles additives in these specific oils.

5.3 Analysis and testing of structure-properties-application relationship *(University of Arkansas subcontract)*

The University of Arkansas investigates the effects of nanolubricants addition into motor, gear oils and military gear oil using a pin-on-disc test and test vehicle based on real gearbox housing (FZG test) and evaluate its performance.

<u>Pin/ball-on-disk tribotesting</u>

Motor and gear oils with nanoparticles have been submitted for tribological studies. Testing has been started with the pin/ball-on-disk tribometer. The Stribeck curve was chosen as a method to compare the performance of the oils. This will allow for comparison of performance at different lubrication regimes. To generate the curve several test stages are performed using the same sample and wear track. Each stage has a duration of five minutes at the following decreasing surface speeds then back up again: 12 cm/s, 10 cm/s, 8 cm/s, 4 cm/s, 2 cm/s, 1 cm/s, 0.5 cm/s , 0.25 cm/s, and 0.13 cm/s.

Complementary analytical techniques will be used to fundamentally understand behavior of the NanoGlide unique chemistries in tribofilms. The diagnosis of the above nanolubricants will involve chemical and structural analysis (XPS and TEM) for tribological behavior on pin/ball-on-disc. The University of Arkansas explores an active partnership with a leading Tribology group at the Naval Research Laboratory (NRL). The University of Arkansas will collaborate, through exchange of student, with Dr. Kathryn J. Wahl (NRL) in using a specially designed instrument at NRL for *in situ* friction and wear analysis. This tribology approach will allow learning behavior of nanolubricant at the nanoscale loading contact plastic behavior of nanoparticles using an optically transparent pin/ball. Raman signal tapped through the optically transparent pin/ball will carry the chemical signature of the event as it is occurring. This will give first hand insight in fundamental mechanism for behavior of the above novel chemistries.

<u>Design of gear testing set-up for the study of lubricant performance</u>

Gears like other mechanisms have specific lubrication needs due to their high point loading. This contact pressure is much higher than that experienced by crankshaft journals and piston cylinders in an engine; therefore higher weight oils are used. Even with these high viscosity oils, at higher loads gears still undergo boundary lubrication. In this condition the pressure between the two surfaces is so high that the fluid is squeezed out of the way and the surfaces come in contact. This metal to metal contact increases the wear and friction, reducing the life of the part. For this reason solid particle additives can be used to avoid the surface to surface contact. The particles floating in the oil will become deposited between the asperities of the surface and aid in lubrication.

The pin-on-disk and four ball tests only account for the sliding friction in the gear pairs. At tooth interface, the surfaces in contact change angle while sliding occurs resulting in both a rolling and sliding friction mechanism during operation. Also, the gear tooth contact is a non-continuous process and both tests discussed above are continuous. Because of these differences there can be discrepancies in results from bench testing to real world performance.

For gear applications the FZG is the most effective large scale test; the rig consists of a motor that drives two shafts by a slave gear box. One shaft has a torque measuring instrument and the other a loading clutch. These two shafts then input to the test gear box. This is illustrated in the Figure 7. The two main standards for this rig are the scuffing test and the pitting test. The scuffing test uses profile A gear specimens and consists of loading stages. The rpm is constant at 1400 rpm and run for 15min on each stage with increasing load. When the wear scar on all teeth covers the tooth width the test is complete. The pitting test uses profile C gear specimens and is performed at a constant rpm and load until 4% of the tooth area is pitted [6].

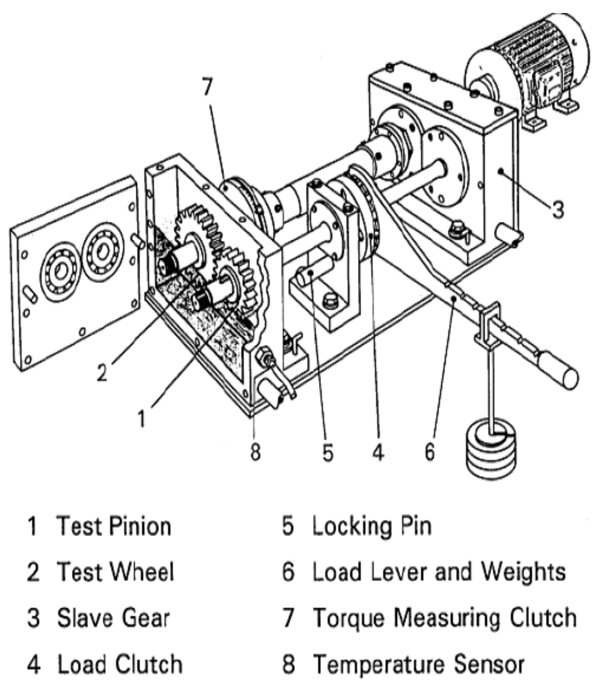

Figure 7. FZG test [6]

The FZG rig can also be used to measure the power loss of the gear oil. One method is to perform several no load runs at different speeds, then several load runs at the same speeds. During those runs measurements of the motor torque and speed or electrical consumption of the motor is taken to get the power comparison. The no load runs will give the windage loss from the gears churning in the oil and the load runs will give the losses from the tooth interfaces.

Figure 8 shows the outline of the design described in this paragraph. A pulley system will be used to convert the 1760 rpm of the motor to the required 1440 rpm of the test procedure. This will then be connected to the slave gears. Also, due to the tension of the pulleys this gearbox will have a larger bending stress added to the shaft instead of mostly torsion stress. This will increase the required shaft and bearing size of the gearbox. Then the gearbox is connected to the clutches using LoveJoy spider couplers to absorb any unwanted vibrations and slight misalignment. The system will be mounted to a heavy cart for mobility but can be locked down during testing.

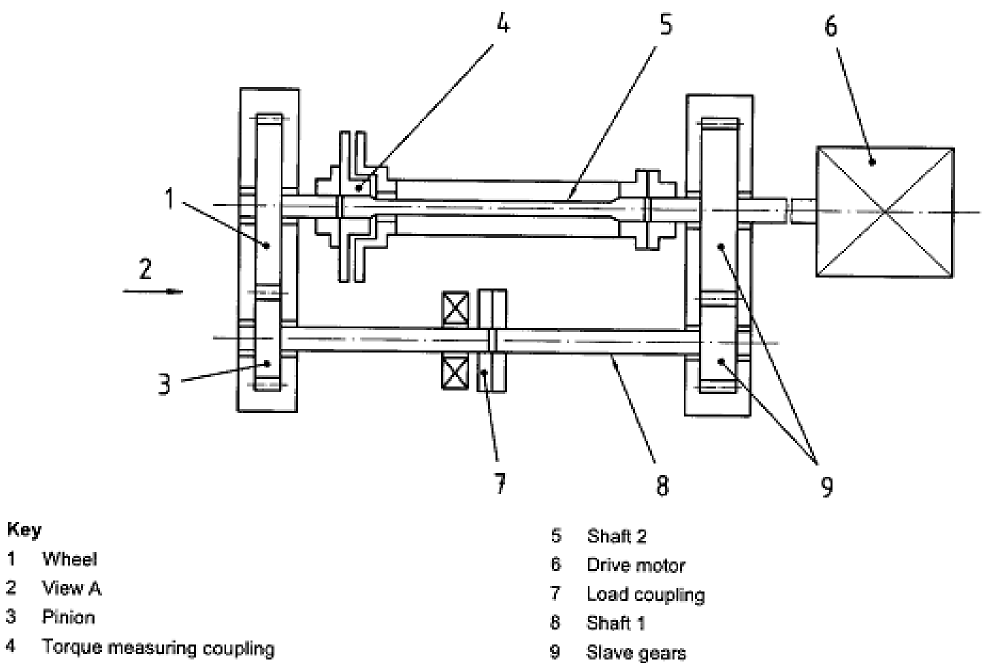

Figure 8. Schematic section of the FZG gear test machine [6]

Currently, a parts list of the required main materials is developed for the build, and parts are in the process of purchasing. The required shaft and bearing sizes are in the process of calculating for long service life given the motor output and required pinion torque.

<u>Deliverables</u>

Accomplished deliverables:

1. Design of experiments for tribological testing;

2. Tribological testing of NanoGlide samples in motor oils using 4 ball test, EP 4 ball test;

3. Tribological testing of NanoGlide samples in military oils using WAM test;

4. Design of FZG gear test machine

Deliverables for 3rd quarters of the project:

1. Tribological testing of NanoGlide samples in motor and engine oils using pin/ball-on-disc, and engine oil using 4 ball test and EP 4 ball test];
2. Tribological testing of NanoGlide using a test vehicle based on real gearbox housing;
3. Travel to NRL for studying *in situ* friction and wear behavior;
4. Investigating the effects of nanolubricants addition into regular military gear oil and their tribological performance;
5. Understanding of nanolubricant behavior at the nanoscale loading contact;

Conclusions

NanoGlide lubricants address the diverse application needs of Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to “dry and harsh” conditions and deliver tribofilm as a result of plastic deformation, when trapped among asperities. Such application components of interest to the Navy, for on- and off- shore purposes, are bearings, gear boxes, and engines.

Two formulations are developed for lubrication applications (additives to motor and gear oils, and greases). The inorganic core/carrier consists of molybdenum disulfide (MoS_2) and organic molecular chemistries for integration include dialkyl dithiophosphate groups (DDP) or environmentally benign canola oil/phospholipid molecules.

In the second quarter of this project, developed nanolubricants were selected and synthesized for application as additives in motor oils, gear oils and greases. Synthesis, characterization, and optimization of developed nanolubricant formulations (NanoGlide®) prepared by laboratory bench process were finalized. Properties of these nanolubricants were investigated through chemical, structural, and tribological analysis. During the synthesis and optimization process one of the main objectives is to reduce milling time and obtain predictability in particle size, integration of additional functional groups and capping consistency and uniformity of nanoparticle dispersion in oils, which will further increase the efficiency and reduce the cost of nanolubricant making.

NanoGlide® production procedures and Design of Experiments (DoE) for synthesis and optimization using scale up were developed. De-agglomeration and optimization studies of synthesized nanolubricant formulations are in progress and on schedule for process scale up and nanomanufacturing of NanoGlide®.

Two strategies to validate the NanoGlide nanoparticle performance in oils and collect performance data include comparison of tribological performance for oil without nanoparticle addition and with nanoparticles and comparison of tribological performance for oils with higher viscosity without nanoparticles and oils with lower viscosity with nanoparticles. Design of experiments for tribological testing of nanolubricant in motor and gear oil, and greases was developed and finalized. Tribological testing of NanoGlide® samples in motor oils using 4 ball test, EP 4 ball test was performed, and their performance, comparison, and evaluation are presented and discussed in this report.

The feasibility lubrication testing of NanoGlide® samples in military oils was evaluated using WAM test and competition/synergy between additive package in formulated military-certified oils and nanoparticle additives was explored. Design of gear testing (FZG test) and parts list of the required main materials for the set up is developed and is in the process of building.

References

1. Malshe, A., Verma, A. (January 2006), Nanoparticles Based Lubricants, Patent Pending.
2. Malshe, A., Verma, A. (July 2006), Active Nanoparticles: Synthesis, Behavior And Applications, Patent Pending.
3. Verma, A., Jiang, W., Abu Safe, H., Brown, W., Malshe, A. (2008), Tribological Behavior of Deagglomerated *Active* Inorganic Nanoparticles for Advanced Lubrication, Tribology Transactions, 51 (5), 673.
4. Komvopoulos, K., Pernama, S.A.; Ma, J.; Yamaguchi, E.S.; Ryason, P.R. (2005), Synergistic Effects of Boron-, Sulfur-, And Phosphorus-Containing Lubricants in Boundary Lubrication of Steel Surfaces Tribology Transactions, 48 (2), 218.
5. WAM, Wedeven Associates, Inc., www.wedeven.com
6. ISO 14635-1, FZG test method A/8,3/90 for relative scuffing load carrying capacity of oils.

Cost and financial status

	Budget	Actual Q1	Actual Q2	Total
NanoMech LLC	$707,727	$77,374.25	$110,288.44	$187,662.49
University of Arkansas	$61,261	$0	$0	$0
Total costs	$768,988	$77,374.25	$110,288.44	$187,662.49

Publications and presentations:

The 65th STLE (Society of Tribology and Lubrication Engineers) Annual meeting and exhibition was attended in May 2010 and a general paper by group of authors (Ajay Malshe, Dmytro Demydov, Atanu Adhvaryu, Philip McCluskey, and Ali Erdemir) was presented in Nanotribology section entitled "Advanced Nanolubricants Additives for Formulated Oils." The main objectives at this meeting was to connect with the potential customers / partners, determine which standards they need to work to (additive and / or final formulation) and pick the most receptive partners.

Appendix A: Project Plan Timeline

Table A1. Technical Tasks

	Tasks	**MONTH 1-2**	**MONTH 3-4**	**MONTH 5-6**	**MONTH 7-8**	**MONTH 9-10**	**MONTH 11-12**
1.	***Designing of application-specific active nanolubricant (NanoGlide)***						
2.	***Process scale up and nanomanufacturing NanoGlide***						
3.	***Synthesis, de-agglomeration and optimization of NanoGlide***						
4.	***Structural, chemical and physical analysis of NanoGlide***						
5.	***Tribological testing of NanoGlide***						
6.	***Commercialization of NanoGlide***						

Appendix B: Coefficient of friction for 4 Ball test of NanoGlide in motor oils

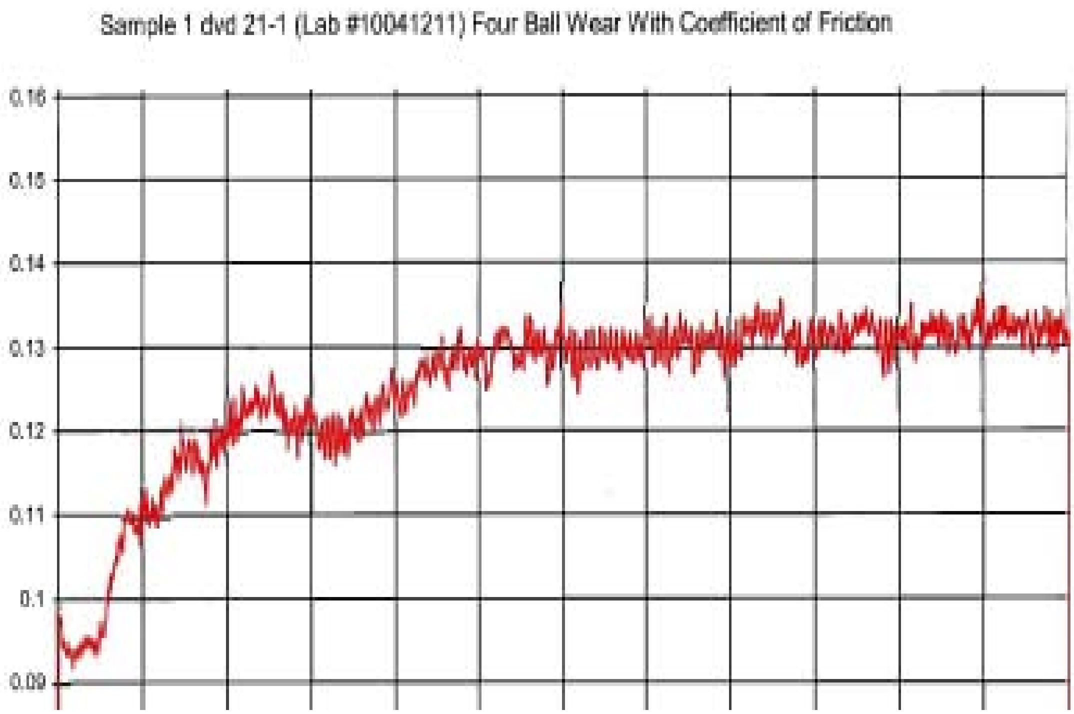

Figure B.1. Four ball test Coefficient of friction for Motor Oil “A” Neat

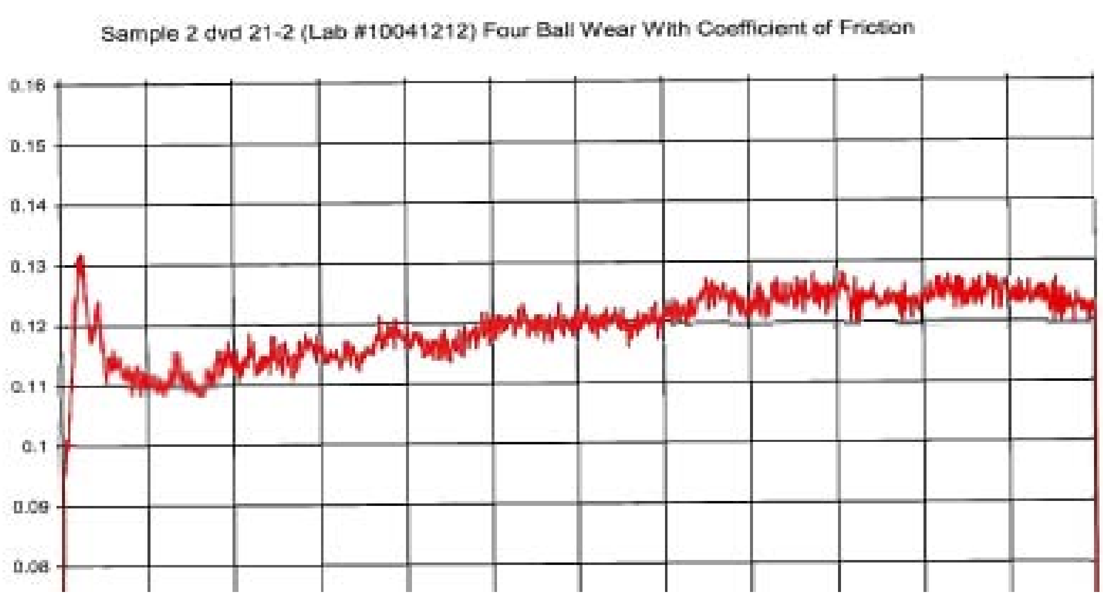

Figure B.2. Four ball test Coefficient of friction for Motor Oil “B” Neat

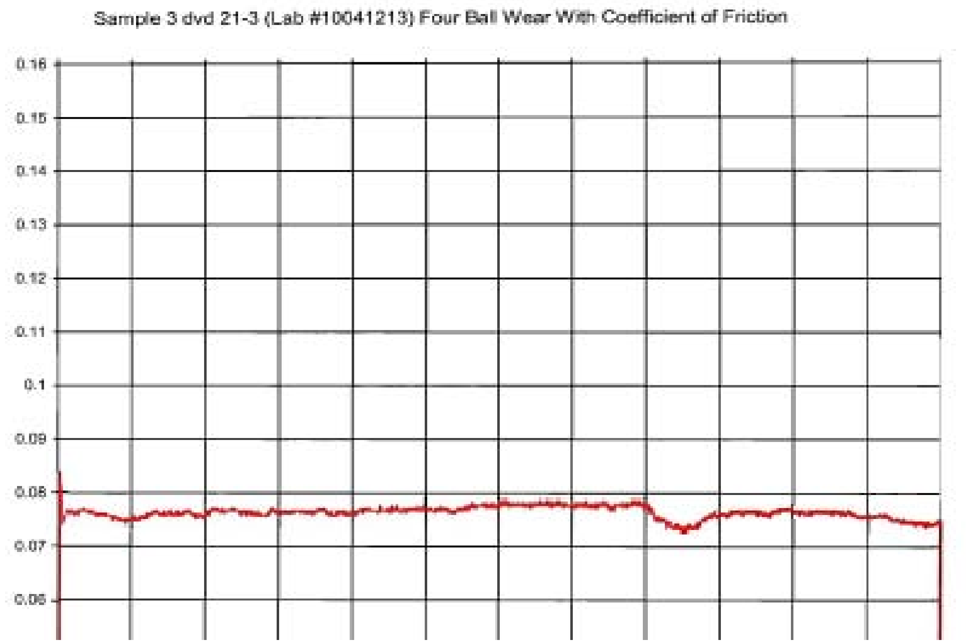

Figure B.3. Four ball test Coefficient of friction of Motor Oil “A” Formula Complete

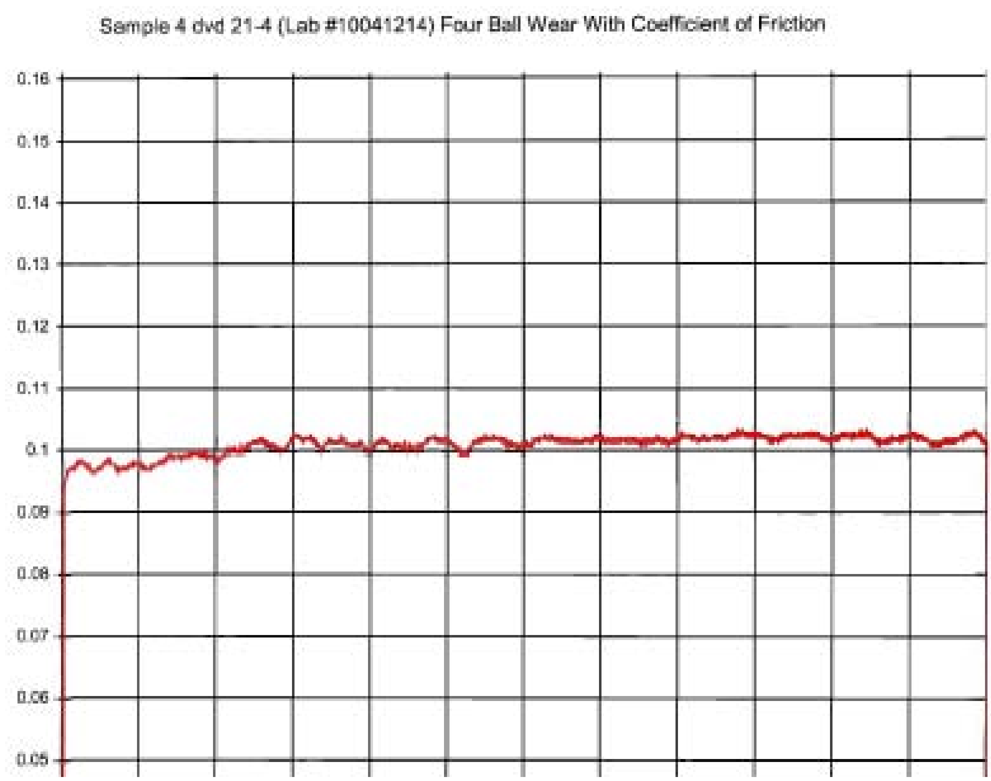

Figure B.4. Four ball test Coefficient of friction of Motor Oil “A” Formula Complete minus MoS_2 (without friction modifier additive)

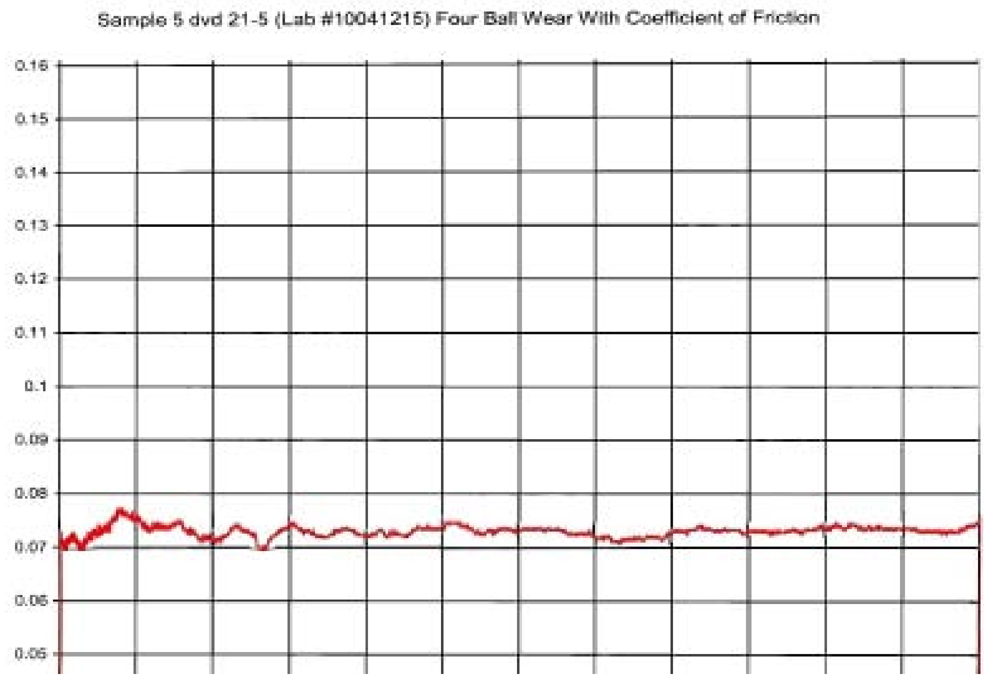

Figure B.5. Four ball test Coefficient of friction of Motor Oil "B" Formula Complete minus MoS_2 (without friction modifier additive)

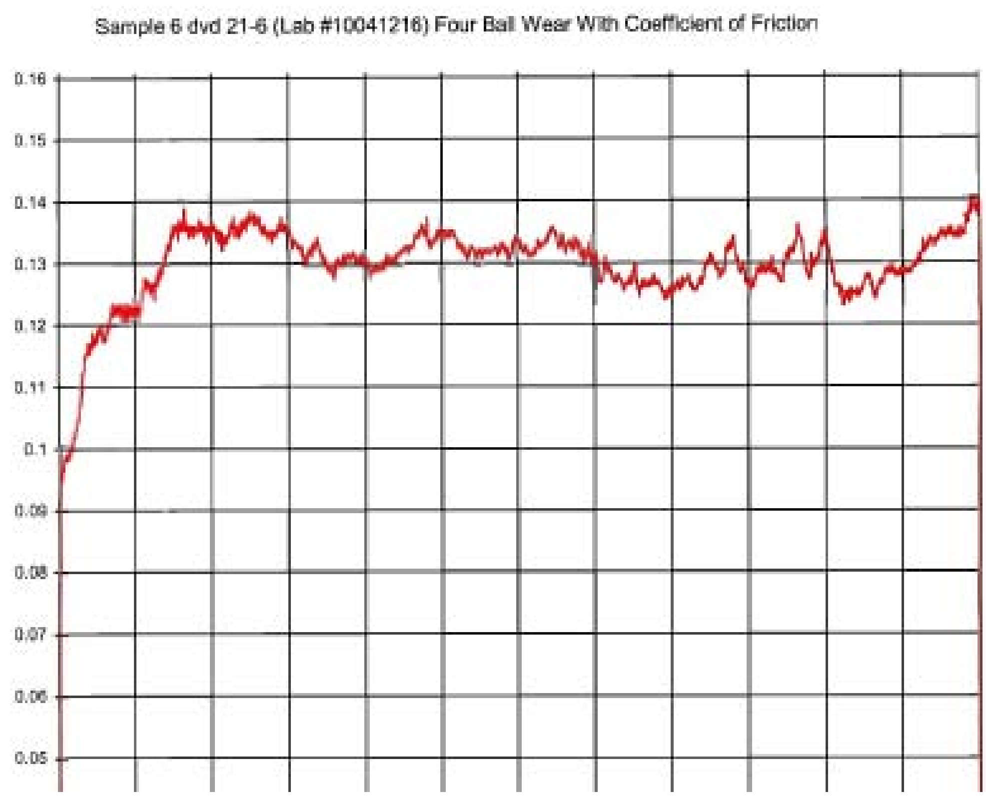

Figure B.6. Four ball test Coefficient of friction of Motor Oil "A" Neat with NanoGlide nanoparticle

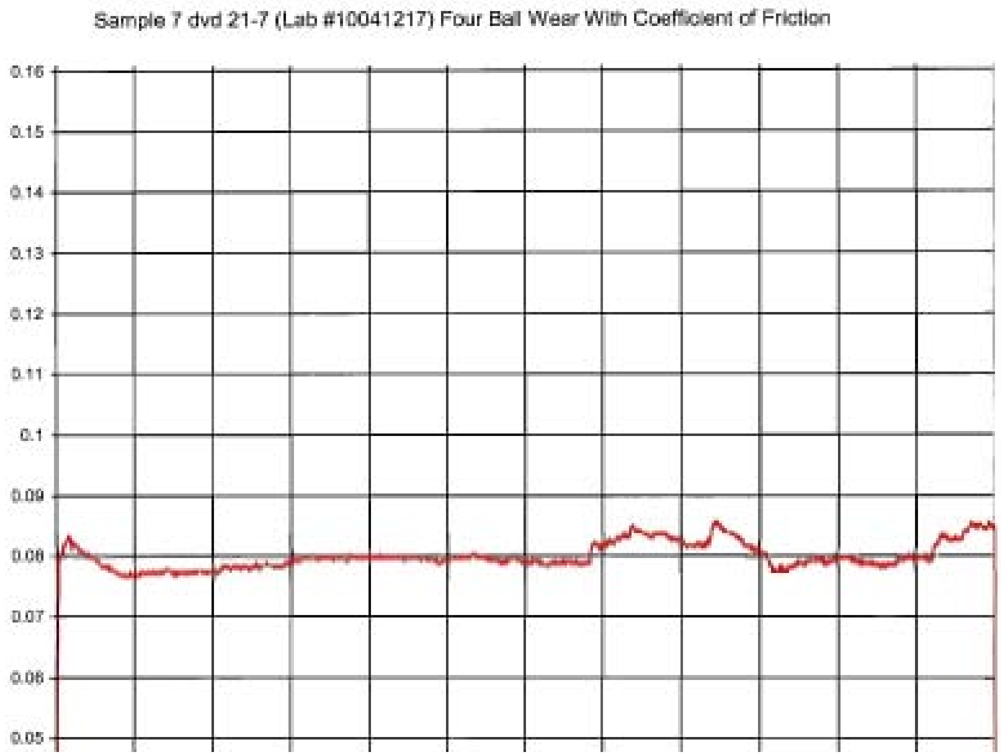

Figure B.7. Four ball test Coefficient of friction of Motor Oil "A" Formula complete with NanoGlide nanoparticle

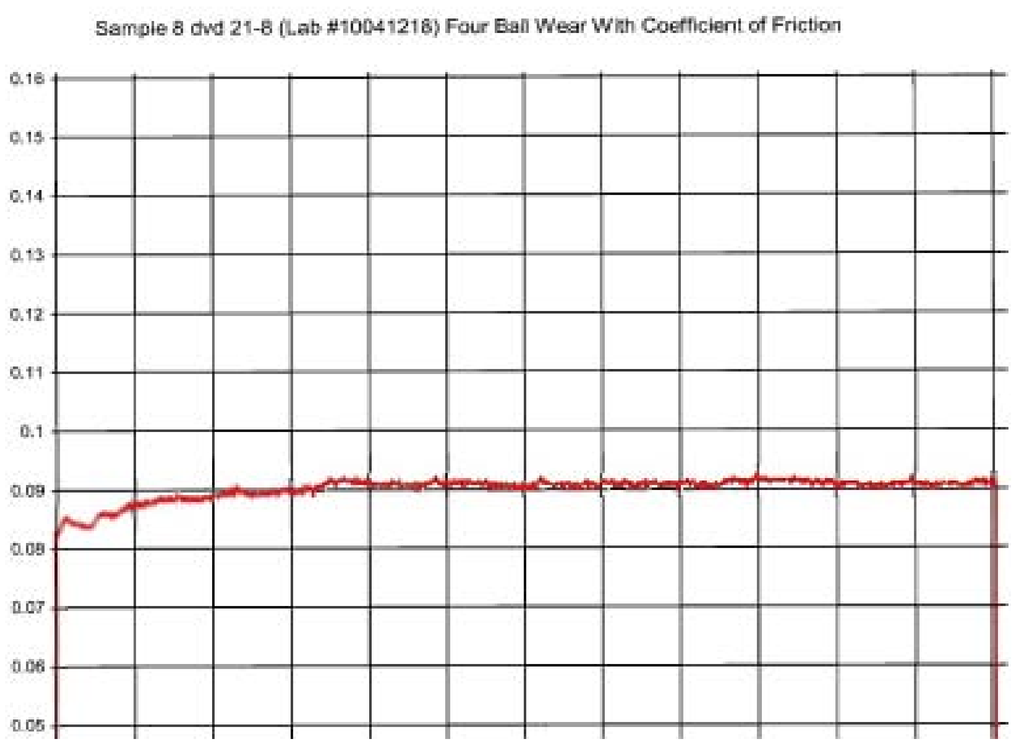

Figure B.8. Four ball test Coefficient of friction of Motor Oil "A" Formula Complete minus MoS_2 (without friction modifier additive) with NanoGlide nanoparticle

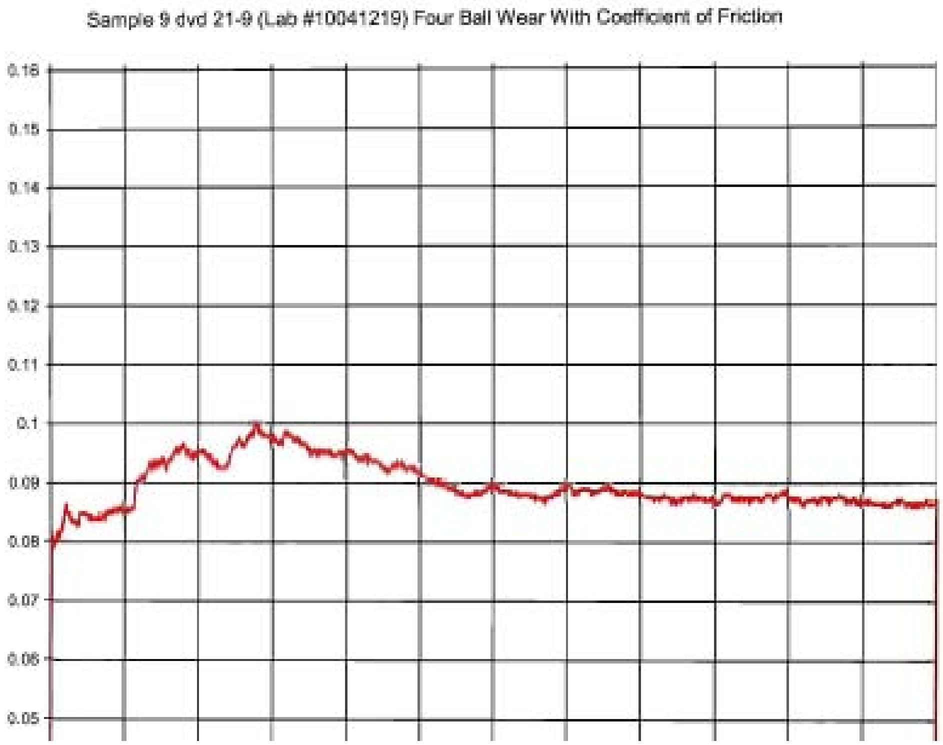

Figure B.9. Four ball test Coefficient of friction of Motor Oil "B" Formula Complete minus MoS_2 (without friction modifier additive) with NanoGlide nanoparticle

Figure B.10. Four ball test Coefficient of friction of Motor Oil "B" Formula Complete minus MoS_2 (without friction modifier additive) with W_2 nanoparticle

Appendix C: WAM Testing

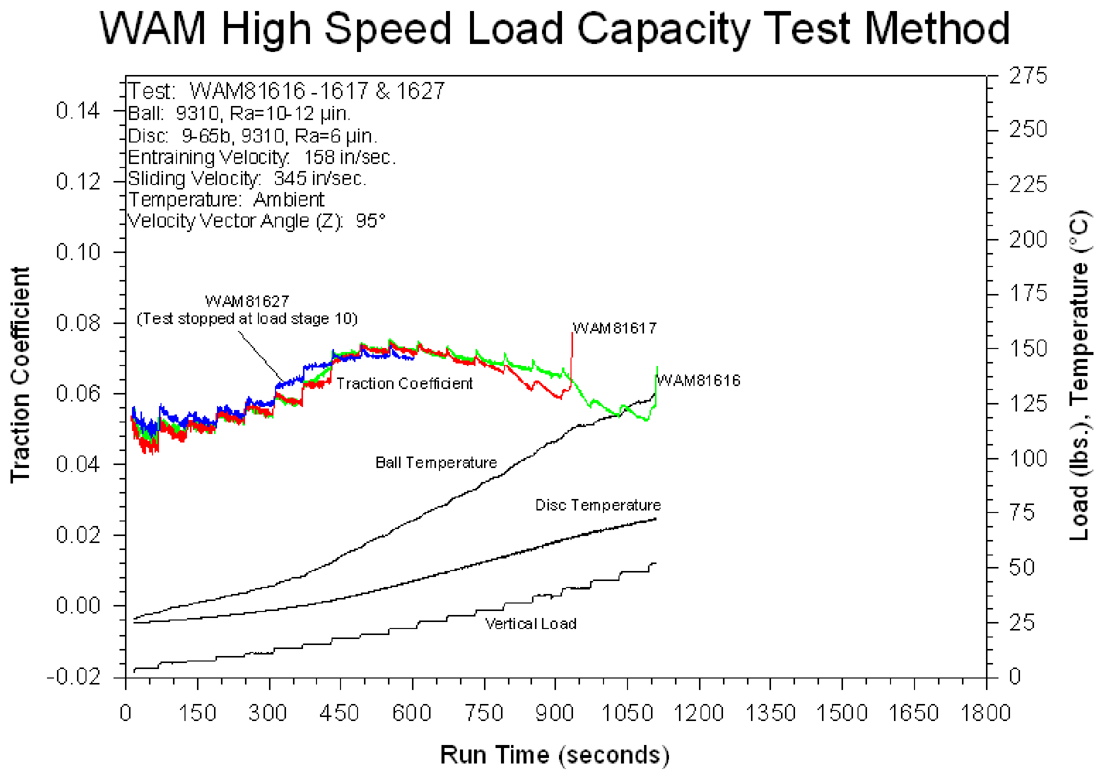

Figure C.1. WAM testing of "M1" oil

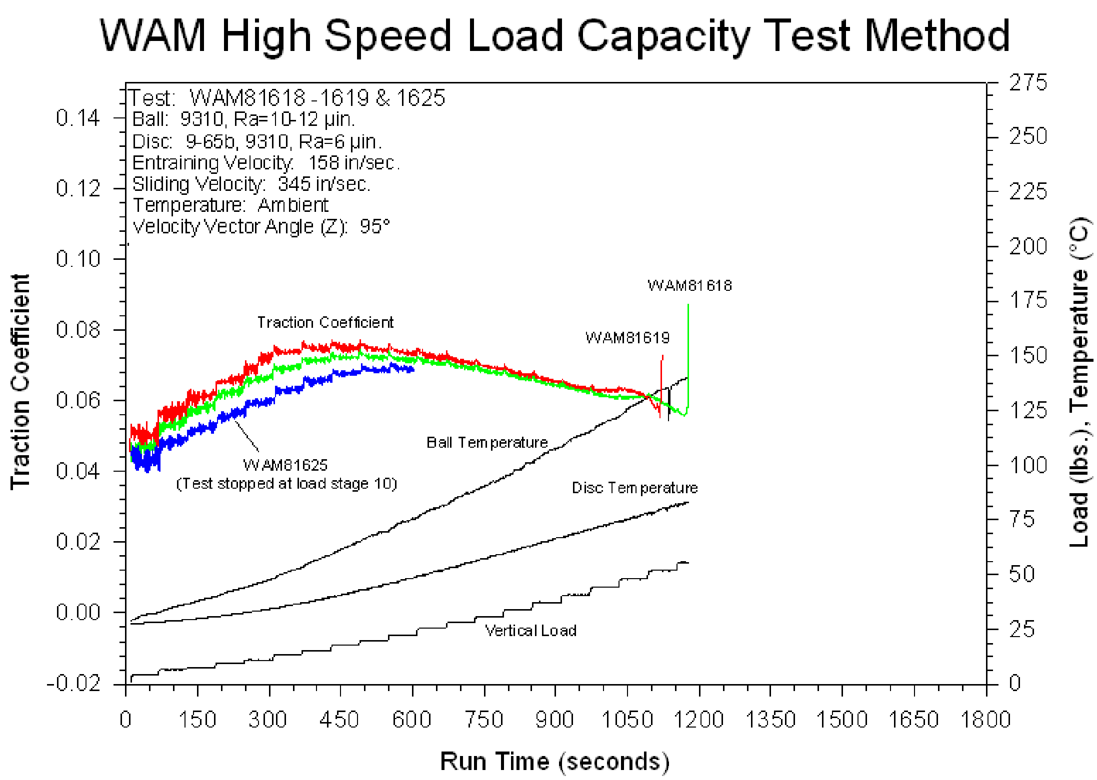

Figure C.2. WAM testing of "M2" oil

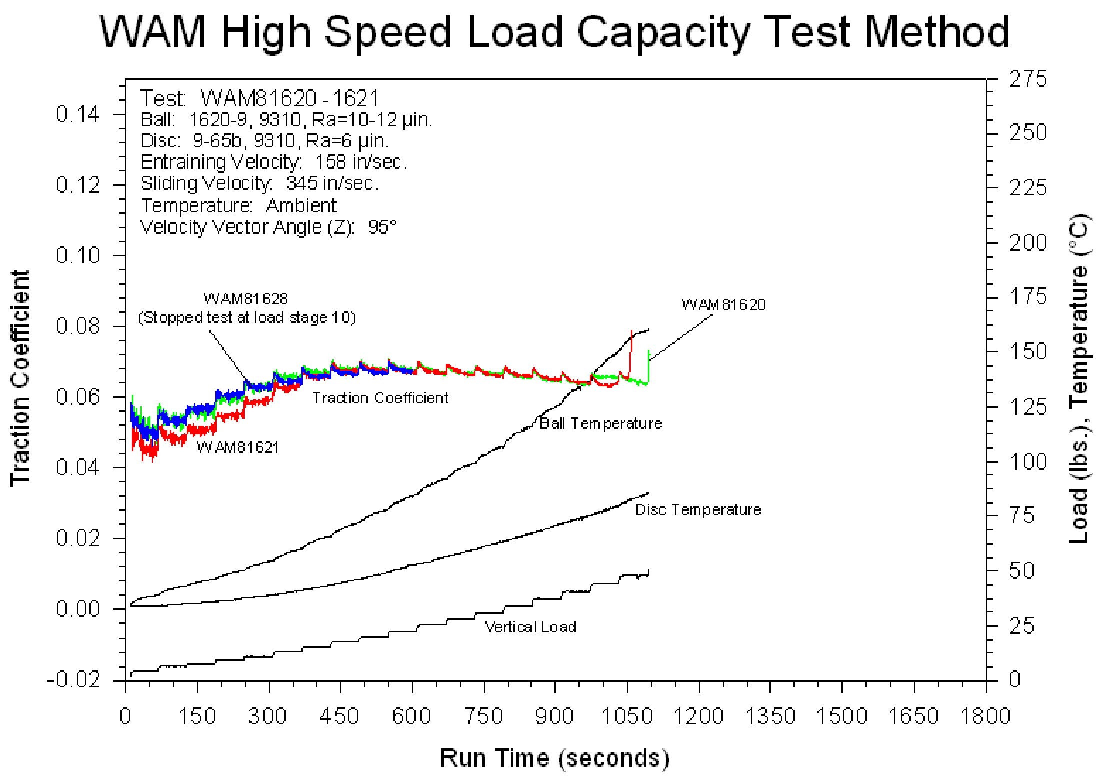

Figure C.3. WAM testing of "M1" oil with MoS_2 nanoparticles (NanoGlide)

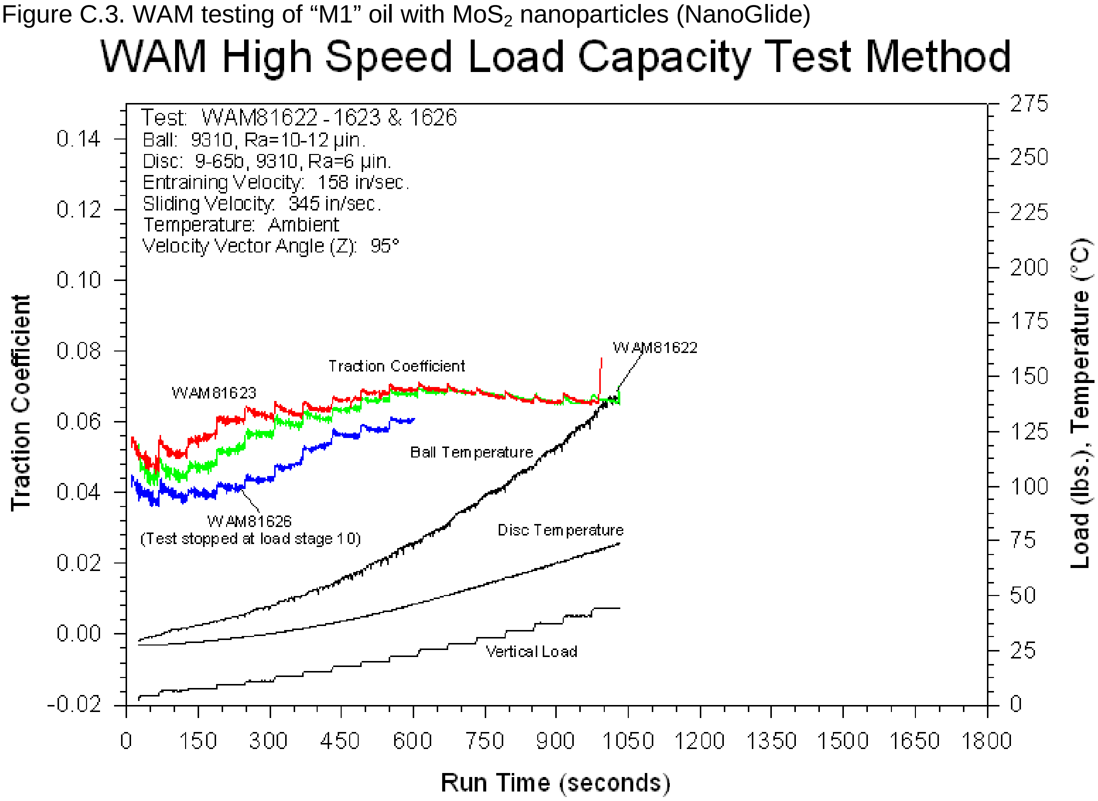

Figure C.4. WAM testing of "M2" oil with MoS_2 nanoparticles (NanoGlide)